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## Molecular structure and vibrational analysis of 2,4,6-trinitrotoluene and 2,4,6-trinitrotoluene- $\alpha$ -d<sub>3</sub>

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**Abstract** The X-ray structures of 2,4,6-trinitrotoluene and 2,4,6-trinitrotoluene- $\alpha$ -d<sub>3</sub> have been determined at 130 K. The molecular structure and vibrational spectra are calculated by the MNDO-PM3 method, and are in agreement with experimental results. The short intra- and intermolecular hydrogen contacts correlate with the known thermal and ionization degradation pathways of 2,4,6-trinitrotoluene.

### INTRODUCTION

In earlier studies [1-3], the vibrational spectra of 2,4,6-trinitrotoluene (TNT) in solid, liquid, and vapor phases have been compared with vibration frequencies calculated by using semi-empirical quantum mechanical models. The structures predicted theoretically were in reasonable agreement with that found in a room temperature X-ray diffraction study [4] for the average of the two independent molecules (designated forms A and B both here and in Ref. [4]) in the unit cell. The experimental structures, however, showed unreasonably large variations in both the C-C (1.364–1.408 Å) and C-N (1.443–1.496 Å) bond distances, which prompted the low temperature (130 K) redetermination of the crystal structure which we now report. We have also determined the structure of TNT- $\alpha$ -d<sub>3</sub> at 130 K to obtain additional verification on the short inter- and intramolecular hydrogen contacts (potential hydrogen bonds) that were reported in the previous study [4]. Finally, we have recalculated both the predicted molecular structure and the predicted gas-phase vibration spectrum using the MNDO-PM3 [5, 6] method.

### EXPERIMENTAL

The synthesis of 2,4,6-trinitrotoluene and 2,4,6-trinitrotoluene- $\alpha$ -d<sub>3</sub> have been described elsewhere [7]. Crystals of each compound suitable for X-ray analysis were cut from larger ones grown by the slow evaporation of solutions of the compounds in n-propanol (TNT) or n-propanol-OD (TNT-d<sub>3</sub>). Data were collected at 130 K on a low temperature-accessorized Syntex P2<sub>1</sub> diffractometer.

### THEORETICAL

The calculations were accomplished with the MOPAC program [8] using the MNDO-PM3 method [5, 6]. The MNDO-PM3 method uses optimized parameters that represent a considerable im-

provement over those parameters used with AM1 [9] and other semi-empirical methods. Typically, use of these parameters results in a significant decrease in heats of formation errors [6]. All ground state geometries were optimized using the BFGS function minimization procedure [10-13]. The Hessian matrix for the normal coordinate analysis was calculated as described previously [1].

### RESULTS AND DISCUSSION

The heavy atom bond distances and bond angles obtained from the low temperature X-ray structures of 2,4,6-trinitrotoluene and 2,4,6-trinitrotoluene- $\alpha$ -d<sub>3</sub>, and the corresponding dimensions of TNT calculated by the MNDO-PM3 method are given in Tables 1 and 2. The estimated standard deviations of the heavy-atom dimensions are: angles 0.4 (TNT) or 0.4–0.5 (TNT-d<sub>3</sub>); C-C bonds 0.006–0.007 Å (TNT) or 0.007 Å (TNT-d<sub>3</sub>); C-N and N-O bonds 0.005–0.006 Å (TNT) or 0.006–0.007 Å (TNT-d<sub>3</sub>).

In general, the bond distances found in the present low temperature studies are in better agreement with those calculated by the MNDO-PM3 method than are the corresponding distances obtained in the previous room temperature structure determination [4]. The ring C-C bond distances span a much narrower range in the low temperature structures and the C-N bond distances are also closely similar.

The dihedral angles between the ring planes and the nitro groups differ by only a few degrees from those found in the earlier study, as shown in Table 3. The oxygen atoms on the o-nitro groups that are nearest the methyl group lie on the same side of the ring plane. In the calculated structure (gas phase) the 4-nitro group is almost coplanar with the phenyl ring, stabilized by hydrogen interactions as shown in Fig. 1, while those in the 2- and 6-positions are significantly twisted out of this plane.

The present study confirms the existence of the various short intra- and intermolecular hydrogen contacts (hydrogen bonds?) identified in the earlier

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Table 1. Bond distances ( $\text{\AA}$ ) and bond angles (degrees) for form A TNT and TNT- $d_3$ 

Distance*	TNT		TNT- $d_3$		TNT		TNT- $d_3$	
	Obs.	Calc.	Obs.	Angle	Obs.	Calc.	Obs.	
C1-C2	1.509	1.487	1.495	C1-C2-C3	123.7	120.7	123.7	
C2-C3	1.403	1.408	1.394	C2-C3-C4	124.3	121.3	124.5	
C3-C4	1.390	1.395	1.396	C3-C4-C5	117.4	119.9	116.7	
C4-C5	1.378	1.397	1.366	C4-C5-C6	122.7	119.8	123.3	
C5-C6	1.389	1.396	1.372	C5-C6-C7	116.4	119.9	116.7	
C6-C7	1.382	1.396	1.379	C6-C7-C2	125.7	121.3	125.2	
C7-C2	1.399	1.405	1.394	C7-C2-C3	113.6	117.7	113.4	
C3-N1	1.475	1.516	1.470	C2-C3-N1	119.6	121.8	119.9	
C5-N2	1.475	1.510	1.483	C4-C3-N1	116.1	116.9	115.6	
C7-N3	1.475	1.517	1.485	C2-C7-N3	118.9	121.8	118.6	
(N-O) <sub>ave</sub>	1.225(6)	1.211	1.218(9)	C6-C7-N3	115.6	116.9	116.1	
				C4-C5-N2	119.0	119.1	118.0	
				C6-C5-N2	118.3	120.1	118.7	
				(C-N-O) <sub>ave</sub>	117.5(6)	118.5	117.5(9)	
				(O-N-O) <sub>ave</sub>	125.0(3)	123.0	124.9(3)	

\* Atom designations as in Ref. [4].

Table 2. Bond distances ( $\text{\AA}$ ) and bond angles (degrees) for form B TNT and TNT- $d_3$ 

Distance*	TNT		TNT- $d_3$		TNT		TNT- $d_3$	
	Obs.	Calc.	Obs.	Angle	Obs.	Calc.	Obs.	
C8-C9	1.494	1.487	1.492	C8-C9-C10	124.4	120.7	124.9	
C9-C10	1.404	1.408	1.397	C9-C10-C11	124.7	121.3	125.1	
C10-C11	1.380	1.395	1.379	C10-C11-C12	117.4	119.9	117.0	
C11-C12	1.381	1.397	1.390	C11-C12-C13	122.8	119.8	123.0	
C12-C13	1.379	1.396	1.376	C12-C13-C14	116.1	119.9	115.9	
C13-C14	1.375	1.396	1.386	C13-C14-C9	126.4	121.3	126.1	
C14-C9	1.400	1.405	1.403	C14-C9-C10	112.6	117.7	112.9	
C10-N4	1.482	1.516	1.488	C9-C10-N4	119.5	121.8	119.5	
C12-N5	1.467	1.510	1.464	C11-C10-N4	115.8	116.9	115.5	
C14-N6	1.486	1.517	1.474	C9-C14-N6	117.8	121.8	118.0	
(N-O) <sub>ave</sub>	1.228(4)	1.211	1.221(3)	C14-C12-N5	115.8	116.9	115.8	
				C11-C12-N5	119.8	119.1	118.3	
				C13-C12-N5	118.4	120.1	118.6	
				(C-N-O) <sub>ave</sub>	117.4(5)	118.5	117.3(5)	
				(O-N-O) <sub>ave</sub>	125.2(4)	123.0	125.4(8)	

\* Atom designation as in Ref. [4].

Table 3. Dihedral angles (degrees) between nitro groups and the plane of the ring in 2,4,6-trinitrotoluene isotopomers

Molecular form	Nitro group		
	2	4	6
A (Ref. [4])	51	24	43
A (this work)	52.0	22.3	43.4
A- $d_3$ (this work)	51.8	23.0	42.3
B (Ref. [4])	60	30	45
B (this work)	58.7	33.0	39.6
B- $d_3$ (this work)	58.9	33.0	39.5
Calc. (this work)	55.1	9.3	76.2

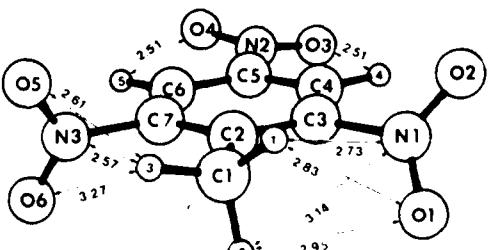


Fig. 1. Calculated molecular structure of 2,4,6-trinitrotoluene. The atom designation is that of TNT structure A in Ref. [4], and distances are in  $\text{\AA}$ .

work. We observe O-H hydrogen contacts between two A molecules (O5 H2) and an A and a B molecule (O4 H10) that approximate distances of 2.5  $\text{\AA}$ . Only the first of these involves the kind of methyl-

hydrogen-to-nitro-oxygen interaction that has been implicated in the thermal degradation of TNT. Of greater significance is the complete lack of hydrogen bonding involving the para-nitro groups. Such

absences are consistent with the *para*-nitro group being unreactive in the thermal or ionization breakdown of TNT [14-16].

Tables 4 and 5 contain the calculated [5, 6] and observed [1, 3] vibration frequencies of TNT and TNT-d<sub>3</sub>. The symmetry designations [1] are based on the nominal C<sub>2v</sub> symmetry of the calculated structure, with the principal axis in the z-direction and the y-direction orthogonal to the plane of the ring. The A<sub>2</sub> and B<sub>1</sub> vibrations are out-of-plane; A<sub>2</sub> vibrations are i.r. inactive if the molecule has genuine C<sub>2v</sub> symmetry, but such is not the case in the present instance and at least some of the A<sub>2</sub>-species vibrations may become observable.

In correlating calculated vibrational frequencies to those observed, emphasis was placed on absorption intensities and isotopic substitution [3]. In the majority of cases, calculated absorption frequencies with large transition dipoles were identified with the more intense absorption bands. The major improvement in the calculations occurs in the NO<sub>2</sub> v<sub>sym</sub> and v<sub>asym</sub> stretching frequencies, where the error compared to previous calculations [3] decreases from 34% to 22%. The C-H stretching frequencies in the 2800-3100 cm<sup>-1</sup> range are reproduced with an average error of 1.3% vs 3.0% using the AM1 method. The remaining frequencies over the range of 400-1800 cm<sup>-1</sup> are reproduced with an average error

Table 4. Observed and calculated frequencies (cm<sup>-1</sup>) for 2,4,6-trinitrotoluene

KBr	Vapour	v <sub>obs</sub> <sup>a</sup>	v <sub>calc</sub>	Symmetry	Assignment†	Transition dipole
465		444	B <sub>1</sub> , B <sub>2</sub>	11, 14		0.10
467		480	B <sub>2</sub>	12		0.28
565		533	B <sub>1</sub>	12		0.34
579		558	B <sub>2</sub>	15		0.21
639		634	A <sub>2</sub>	5, 12		1.40
664		669	A <sub>1</sub>	17		2.37
664		673	A <sub>1</sub>	17		2.10
704, 720	705, 721	743	A <sub>2</sub>	17		0.78
		745	A <sub>2</sub>	15		0.06
735	730	749	B <sub>1</sub>	15		0.56
793	792	769	B <sub>2</sub>	15		1.15
		805	B <sub>1</sub>	15		0.13
		868	A <sub>1</sub>	12		1.21
909, 940	907, 938	939	B <sub>2</sub>	16		1.32
		971	A <sub>2</sub>	13		0.11
		990	B <sub>1</sub>	6		0.10
		995	A <sub>1</sub>	16		1.93
1026	1028, 1067	1032	B <sub>1</sub>	12, 13		0.30
1086	1075	1049	B <sub>2</sub>	4, 6		0.75
1171		1182	A <sub>1</sub>	10		0.40
1208	1217, 1230	1247	B <sub>2</sub>	10, 12		0.12
		1271	A <sub>1</sub>	12		0.05
		1334	B <sub>2</sub>	9		0.19
		1360	A <sub>1</sub>	4		0.15
1356	1352	1581	A <sub>1</sub>	19		5.90
1356	1352	1589	B <sub>2</sub>	19		5.90
1356	1352	1604	A <sub>1</sub>	19		0.80
		1376	B <sub>2</sub>	4		0.09
1406	1420	1414	A <sub>1</sub>	9, 16		0.62
1437, 1466	1437, 1457	1449	A <sub>1</sub>	7, 11		0.28
		1551	B <sub>2</sub>	9		1.43
1541	1508	1918	A <sub>2</sub>	18		3.51
1541	1539	1921	B <sub>2</sub>	18		7.58
1541	1539	1925	B <sub>2</sub>	18		7.26
1603, 1619	1617	1614	A <sub>1</sub>	8, 9		1.12
		1734	B <sub>2</sub>	9		1.19
		1790	A <sub>1</sub>	9		2.67
2955	2901	2983	B <sub>2</sub>	1		0.50
3015	2971	2991	A <sub>1</sub>	1		0.42
3058	2991	3057	B <sub>2</sub>	2		0.25
3087	3085	3070	A <sub>1</sub>	2		0.18
3096	3096	3176	A <sub>1</sub>	3		0.30

\*Data from Ref. [1, 3].

†Assignments of vibrational frequencies: 1. Ring C-H stretch; 2. Methyl C-H asym. stretch; 3. Methyl C-H sym. stretch; 4. Methyl H-C-H asym. bend; 5. Methyl H-C-H sym. bend; 6. Methyl rock; 7. Methyl umbrella; 8. C-C stretch: methyl to ring; 9. C-C ring stretch; 10. Ring H-C-C in plane bend; 11. Methyl ring CCC in-plane bend; 12. Ring CCC bend; 13. Out-of-plane bend of ring H; 14. Out-of-plane bend of methyl C; 15. C-N bend; 16. C-N stretch; 17. C-N-O bend; 18. NO<sub>2</sub> asym. stretch; 19. NO<sub>2</sub> sym. stretch.

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Table 5. Observed and calculated frequencies ( $\text{cm}^{-1}$ ) for 2,4,6-trinitrotoluene- $\alpha$ -d<sub>3</sub>

KBr	$v_{\text{obs}}$	$v_{\text{calc}}$	Symmetry	Assignment†	Transition dipole
457, 471		465	$B_1$	12	0.30
563		527	$B_1$	12	0.29
573		554	$B_2$	15	0.20
625		623	$A_1$	5, 15	1.28
677		666	$B_2$	15	1.65
677		672	$B_1$	15	2.35
718	718	694	$A_2, B_2$	4	0.41
733	731	730	$A_2$	17	0.68
—	749	743	$A_1$	17	0.86
758	758	749	$A_2$	15	0.65
775	778	769	$B_1$	15	0.84
826	826	804	$A_1$	15	0.84
826	826	819	$B_2$	15	0.79
872, 909	907	894	$B_1$	12	0.19
938	938	971	$A_2$	13	0.13
938	938	982	$B_2$	16	2.51
938	938	989	$A_1$	16	2.49
1030		1009	$B_1$	13	0.23
1030		1017	$B_1$	13	0.31
1030		1025	$B_1$	4	0.35
1057, 1095	1057, 1067	1070	$A_1$	7	0.09
1179, 1198		1186	$A_1$	10	0.40
1219, 1264	1254	1245	$B_2$	10	0.14
1302		1307	$A_1$	8	0.17
		1333	$B_2$	9	0.18
1354	1352	1581	$A_1$	19	5.89
1354	1352	1589	$B_2$	19	5.91
1354	1352	1604	$A_1$	19	0.85
1410		1418	$A_1$	9, 16	1.06
1539	1508	1918	$A_2$	18	3.50
1541	1539	1921	$B_2$	18	7.61
1541	1539	1925	$B_2$	18	7.23
1599		1550	$B_2$	9	1.46
1619		1613	$A_1$	8, 9	1.13
		1768	$B_2$	9	1.21
		1790	$A_1$	19	2.67
2275		2258	$B_1$	2	0.38
2325		2273	$B_2$	2	0.22
2325		2293	$A_1$	3	0.26
3058	2907	2983	$B_2$	1	0.50
3096, 3087	2971	2991	$A_1$	1	0.42

\*Data from Refs [1, 3].

†Assignments of vibrational frequencies. See Table 4.

of less than  $21 \text{ cm}^{-1}$ , down slightly from the  $24 \text{ cm}^{-1}$  with the AM1 method [3].\*

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